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Ideal adsorbed solution theory solved with direct search minimisation

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Abstract

The ideal adsorbed solution theory (IAST) is the most widespread theory for multicomponent adsorption interpretation. It postulates the existence of an adsorbed phase which behaves as a Raoult ideal solution. The theory results in a system of nonlinear algebraic equations which are solved to know the composition of the adsorbed mixture at equilibrium. In this paper an investigation on an alternative method for the IAST equations solution is proposed which is based on the minimisation of an objective function representing the iso-spreading pressure condition. This approach to the solution of the IAST equations reduces in some cases the computational effort and mitigate the issues of the currently adopted approaches (inversion of functions and initial guess). For binary systems, direct search minimisation approach is faster than the classic IAST equations solution approach up to 19.0 (Dual Langmuir isotherm) and 22.7 times (Toth isotherm). In ternary systems, this difference decreases to 10.4 (O'Brien and Myers isotherm). Compared to FASTIAS approach, direct search minimisation is up to 4.2 times slower in ternary systems

Keywords: *ideal adsorbed solution theory; adsorption equilibria; adsorption thermodynamics; solution algorithm;*

Introduction

Adsorption materials are increasingly attracting interest because they permit almost selectively the separation of targeted compounds, often reducing energy consumption compared with traditional separation techniques. Thanks to their ability of selectively capturing single compounds from complex multicomponent mixtures (Minceva and Rodrigues, 2005) and the suitability of triggering the heat using a concentration swing (Yu et al., 2013), new adsorptive technologies are currently commercialized (Dawoud et al., 2012; Ramaswamy et al. 2013; Santori et al. 2013) or at R&D stage (Liu et al. 2011; Santori et al. 2014). In all cases, adsorption thermodynamics plays a fundamental role in the system design.

In the majority of practical cases, the separation of a selected compound from a multicomponent mixtures is required and consequently multicomponent adsorption thermodynamic theories are regarded with a particular interest. Presently, the most widespread multicomponent adsorption theory is the ideal adsorbed solution theory (IAST) (Myers and Prausnitz, 1965). The reason of its success consists in the possibility to predict multicomponent adsorption equilibrium from single component adsorption isotherms.

In the IAST, an ideal gas phase and an adsorbed phase are in equilibrium. The adsorbed phase is considered an ideal solution following the Raoult's law. In several cases this is an acceptable assumption or can offer a useful initial result for a more refined interpretation (Cessford et al., 2012; Yun et al. 2002).

Multicomponent gaseous mixtures are considered in this paper, but the IAST can be applied similarly to liquid mixtures. The mathematical formulation of the problem consists in the solution of the following algebraic-integral equations:

$$P_{tot} y_i = P_i^0 x_i \quad i = 1, 2, \dots, NC \quad (1)$$

$$\sum_i^{NC} x_i = 1 \quad (2)$$

$$n_i = f_i(P_i^0, T) \quad i = 1, 2, \dots, NC \quad (3)$$

$$\frac{\pi_i A}{RT} = \int_0^{P_i^0} n_i d(\ln(P_i^0)) \quad i = 1, 2, \dots, NC \quad (4)$$

where P_{tot} [kPa] is the total pressure of the gaseous mixture flowing on the adsorbent surface, y_i is the molar fraction of the component i of the non-adsorbed mixture, x_i is the molar fraction of the component i in the

adsorbed phase, NC is the total number of components, q_i^0 [mol/kg] is the specific adsorbed amount of the component i at equilibrium, P_i^0 [kPa] is the surface pressure of the component i , T [K] is the equilibrium temperature, π_i [kPa m] is the specific spreading pressure of the component i , A [m²/kg] is the specific surface area covered by the adsorbed mixture. For the solution of the eqns (1-4) the condition of thermodynamic equilibrium must be considered. The system is at equilibrium when the reduced spreading pressure ($\pi_i A / (RT)$) has the same value for each component. So the equilibrium condition is represented by the following iso-spreading pressure condition:

$$\frac{\pi_i A}{RT} = \text{constant} \quad i = 1, 2, \dots, NC \quad (5)$$

The problem can be solved giving P_{tot} , y_i and the adsorption isotherms $f_i(P_i^0, T)$ with parameters computed by single component adsorption equilibrium data. The unknowns of the system are x_i , π_i , P_i^0 and q_i^0 .

An extensive review of the different approaches proposed for the solution of the problem above has been presented in [8], highlighting the following main issues of the described strategies:

- 1) An inversion of the spreading pressure function is needed and only in few cases such inversion is analytical;
- 2) An initial guess should be provided in order to find a solution.

These issues are overcome following the method proposed in (Rubiera Landa et al., 2013). The only claimed limit of the procedure in (Rubiera Landa et al., 2013) consists in the computational load, which is comparable with the classical solution approaches (Do, 1998; Myers and Valenzuela 1986; Valenzuela and Myers 1989), making the method (FASTIAS) presented in (O'Brien and Myers, 1985) and successively refined in (O'Brien and Myers, 1988) still the quickest numerical method for the solution of IAST equations. In some cases explicit solution of the IAST equations can be formulated for binary systems. In (Le Van and Vermeulen, 1981) a method is presented for deriving explicit binary isotherms from simple single isotherm (Langmuir and Freundlich) in form of series expansions.

Assuming single isotherms fitted considering equal saturation capacities, binary adsorption isotherms have been derived for Brunauer-Emmet-Teller (BET)-Langmuir, BET-BET, Langmuir-Langmuir, anti-Langmuir-anti-Langmuir and quadratic-quadratic (Gritti and Guiochon, 2003a; Gritti and Guiochon, 2003b; Taradafer and Mazzotti, 2012). In addition, explicit isotherms have been derived also without the previous assumption (Frey and Rodrigues, 1994; Ilic et al., 2010).

Integration of IAST equations with adsorptive bed dynamics equations is an additional issue. There are three possibilities to couple IAST equations in adsorptive bed dynamics. Firstly, the spreading pressure can be treated as a dependent variable of time and space and added to the differential system describing bed dynamics (Mota and Rodrigo, 2000). This results in a strongly non-linear system of differential-algebraic equations which is difficult to solve, computationally expensive and time consuming. For this reason the most common methodology consists on the computation of the adsorption equilibrium separately to bed dynamics in each time step. Also the approach is time consuming because it obliges to exit and enter continuously the IAST equations solver with new conditions. The third strategy is the use of the B-Spline approach (Santos et al. 2011). It allows to pre-compute the equilibrium states and this can mitigate the issues for the binary system case, but for more than two components the B-Spline approach results in additional multidimensional fitting issues, losing its advantages.

This paper presents an investigation on the solution of the IAST equations using analytical expression of the spreading pressures for the adsorbed components and a direct search minimisation approach for the iso-spreading pressure condition of eq. (5). The method is tested on a number of adsorption isotherms and on binary and ternary systems.

The immediate way to implement direct search methods for adsorptive bed dynamics is the use of a separate solver. The proposed investigation is not a contribution to the solution of these issues, which are still open.

On the basis of the reported results, direct search methods are expected to reduce the time spent for equilibrium calculations in comparison with the traditional IAST method and consequently the overall bed dynamics simulation times.

2. Solution of the IAST equations through direct search minimisation methods

The IAST equation system can be reduced through successive substitution of variables to a smaller system of iso-spreading pressure conditions. Table 1 shows the analytically integrated form of the spreading pressure for some adsorption isotherms. The spreading pressure are expressed in terms of molar fractions x_i through a preliminary change of variable from P_i^0 to x_i substituting the eq. (1) into eq. (4).

For sake of clarity, taking the Dual Langmuir isotherm, spreading pressure in terms of molar fraction is obtained by the following change of variable:

$$d \ln \left(\frac{P_{tot} y_i}{x_i} \right) = - \frac{1}{x_i} dx_i \quad (6)$$

Accordingly, the spreading pressure integral becomes:

$$\begin{aligned} \frac{\pi_i A}{RT} &= \int - \left(\frac{q_{s1,i} b_{1,i} \left(\frac{P_{tot} y_i}{x_i} \right)}{x_i + x_i b_{1,i} \left(\frac{P_{tot} y_i}{x_i} \right)} + \frac{q_{s2,i} b_{2,i} \left(\frac{P_{tot} y_i}{x_i} \right)}{x_i + x_i b_{2,i} \left(\frac{P_{tot} y_i}{x_i} \right)} \right) dx_i = \\ &= \int \left(- \frac{q_{s1,i} + q_{s2,i}}{x_i} + \frac{q_{s1,i}}{x_i + P_{tot} y_i b_{1,i}} + \frac{q_{s2,i}}{x_i + P_{tot} y_i b_{2,i}} \right) dx_i \end{aligned} \quad (7)$$

The integration of eq. (7) results in the expression listed in Table 1 for Dual Langmuir isotherm. An additional result of this paper is represented by the analytical expression for spreading pressure of the Unilan isotherm, which was deemed not computable (Do, 1998).

Table1: List of the analytical expressions of the spreading pressure for different adsorption isotherms

	Isotherm	Reduced Spreading Pressure
Dual Langmuir	$q_i = q_{s1,i} \frac{b_{1,i} P}{1 + b_{1,i} P} + q_{s2,i} \frac{b_{2,i} P}{1 + b_{2,i} P}$	$\frac{\pi_i A}{RT} = -(q_{s1,i} + q_{s2,i}) \ln(x_i) + q_{s1,i} \ln(b_{1,i} y_i P_{tot} + x_i) + q_{s2,i} \ln(b_{2,i} y_i P_{tot} + x_i)$
Toth	$q_i = q_{s,i} \frac{b_i P}{[1 + (b_i P)^t]^{1/t}}$	$\frac{\pi_i A}{RT} = \frac{y_i P_{tot} b_i q_{s,i}}{x_i} {}_2F_1 \left(\frac{1}{t}; \frac{1}{t}; 1 + \frac{1}{t}; - \left(\frac{y_i P_{tot} b_i}{x_i} \right)^t \right)$ where ${}_2F_1$ is the Gauss hypergeometric function ${}_2F_1$
Unilan	$q_i = \frac{q_{s,i}}{2s_i} \ln \left(\frac{1 + b_i P e^{s_i}}{1 + b_i P e^{-s_i}} \right)$	$\frac{\pi_i A}{RT} = \frac{q_{s,i}}{2s_i} \left[\ln(x_i) \left(\ln \left(\frac{e^{s_i} (b_i y_i P_{tot} e^{s_i} + x_i)}{b_i y_i P_{tot} + e^{s_i} x_i} \right) - \ln \left(1 + \frac{e^{-s_i} x_i}{b_i y_i P_{tot}} \right) + \ln \left(1 + \frac{e^{s_i} x_i}{b_i y_i P_{tot}} \right) \right) - \dots \right.$ $- Li_2 \left(- \frac{e^{-s_i} x_i}{b_i y_i P_{tot}} \right) + Li_2 \left(- \frac{e^{s_i} x_i}{b_i y_i P_{tot}} \right)]$ where Li_2 is the dilogarithm function
O'Brien-Myers	$q_i = q_{s,i} \left[\frac{b_i P}{1 + b_i P} + \frac{\sigma_i^2 b_i P (1 - b_i P)}{2(1 + b_i P)^3} \right]$	$\frac{\pi_i A}{RT} = \frac{q_{s,i}}{2(b_i y_i P_{tot} + x_i)^2} \left(-b_i \sigma_i^2 y_i P_{tot} x_i + 2(b_i y_i P_{tot} + x_i)^2 \ln(x_i) - \dots \right.$ $- 2(b_i y_i P_{tot} + x_i)^2 \ln(b_i y_i P_{tot} + x_i) \left. \right)$

Using the spreading pressures listed in Table 1, the iso-spreading pressure condition can be set as a minimisation problem. Using eq.(2), the objective function of the minimisation problem becomes for the binary case:

$$f_{binary}(x_1) = \left| \frac{\pi_1(x_1) A}{RT} - \frac{\pi_2(x_1) A}{RT} \right| \quad (8)$$

and for the ternary case:

$$f_{ternary}(x_1, x_2) = \left(\left| \frac{\pi_1(x_1) A}{RT} - \frac{\pi_2(x_2) A}{RT} \right| + \left| \frac{\pi_1(x_1) A}{RT} - \frac{\pi_3(x_1, x_2) A}{RT} \right| \right) \quad (9)$$

Considering the isotherms in Table 1, the resulting objective functions present only a minimum whose coordinates correspond to the equilibrium condition. This feature makes the minimisation problem particularly easy to solve even by direct search local minimisation algorithms.

The advantage in the change of the independent variable of the spreading pressure (from P_i^0 to x_i) consists in the chance of constraining the molar fractions x_i in their feasible interval (0,1). So for the more general ternary case, the optimization problem is stated as:

Minimize the objective function $f_{\text{ternary}}(x_1, x_2)$ subject to constraints $0 < x_1 < 1 - x_2$ and $0 < x_2 < 1 - x_1$

From the solutions of this problem the number of total adsorbed moles is calculated with:

$$\frac{1}{q_{\text{tot}}} = \sum_{i=1}^3 \left(\frac{x_i}{n_i (P_i^0)} \right) \quad (10)$$

All the computations presented in this paper were performed with Nelder-Mead minimisation algorithm (Nelder and Mead, 1965) operated with a working precision of 10^{-8} , which resulted in final residuals ranging between 10^{-7} and 10^{-9} . The residuals are far beneath the accuracy of the experimental values and coherent with the order of magnitude considered by other authors (O'Brien and Myers, 1985; O'Brien and Myers, 1998; Rubiera Landa et al, 2013). The comparisons presented in next sections aim to validate quantitatively the proposed approach.

3. Application to single equilibrium conditions

The minimisation approach is applied only to few case studies due to the limited number of experimental data for binary and ternary systems of acceptable quality. The parameters used for the single component adsorption isotherms are reported in Table 2 and Table 3.

Table 2: Parameters of the single component adsorption isotherms for the binary system Methane(1)/Ethane(2) on activated carbon BPL at 301.4 K (He et al., 2004)

	Pressure Range		Dual Langmuir				Toth	
	[kPa]	q_{s1}	b_1	q_{s2}	b_2	q_s	b	t
Methane	0-3220.7	0.894481	$8.368828 \cdot 10^{-3}$	4.921966	$6.950138 \cdot 10^{-4}$	7.912945	$1.520872 \cdot 10^{-3}$	0.5620853
Ethane	0-791.98	4.698140	$5.876234 \cdot 10^{-3}$	1.173161	$1.683690 \cdot 10^{-1}$	9.382593	$4.406557 \cdot 10^{-2}$	0.3808238

Table 3: Parameters of the single component adsorption isotherms for the ternary system Methane(1)/Nitrogen(2)/Carbon Dioxide(3) on activated carbon Norit R1 at 298 K (Dreisbach et al., 1999) and ternary system Methane(1)/Ethane(2)/Ethylene(3) on activated carbon BPL at 301.4 K (O'Brien and Myers 1985)

	Pressure Range		Unilan			O'Brien-Myers	
	[kPa]	q_s	b	s	q_s	b	σ
Adsorbent: AC Norit R1							
Methane	0-5753	9.280873	$7.544924 \cdot 10^{-4}$	2.000000	--	--	--
Nitrogen	0-5958	6.975740	$3.356512 \cdot 10^{-4}$	1.707017	--	--	--
Carbon Dioxide	0-6000	13.171592	$1.560106 \cdot 10^{-3}$	1.621091	--	--	--
Adsorbent: AC BPL							
Methane	131.7-339.2	--	--	--	5.721	$9.0023 \cdot 10^{-4}$	0.8231
Ethane	131.7-339.2	--	--	--	5.639	$1.0186 \cdot 10^{-2}$	1.1927
Ethylene	131.7-339.2	--	--	--	5.900	$6.4428 \cdot 10^{-3}$	1.1737

3.1 Binary systems

The adsorption of the binary system Methane(1)/Ethane(2) in BPL activated carbon is analysed, regressing the data with Dual Langmuir (DL) and Toth isotherms adopting parameters of Table 2. Table 4 shows a comparison of the experimental data with the equilibria predicted by IAST using same isotherms (DL-DL or Toth-Toth) for both the components.

Table 4: Methane(1)/Ethane(2) adsorption in BPL Activated Carbon at 301.4 K (He et al., 2004). Experimental data and results from the calculation of IAST equations using DL and Toth isotherms

Pressure [kPa]	y_1	exp. data	$q_1 (x_1)$		$q_2 (x_2)$		Calculation Times [s]			
			DL	Toth	DL	Toth	DL		Toth	
							min IAST	trad. IAST	min IAST	trad. IAST
52.02	0.716	0.158 (0.119)	0.166 (0.127)	0.165 (0.124)	-5.3 (-6.6)	-4.0 (-4.5)	0.032	0.438	0.047	0.566
197.05	0.716	0.347 (0.139)	0.361 (0.149)	0.358 (0.144)	-4.1 (-6.9)	-3.0 (-3.5)	0.031	0.566	0.031	0.703
682.61	0.716	0.673 (0.174)	0.649 (0.166)	0.624 (0.162)	3.6 (4.6)	7.8 (6.9)	0.031	0.660	0.062	0.701
1397.62	0.716	0.853 (0.187)	0.801 (0.172)	0.799 (0.172)	6.1 (8.2)	6.7 (8.4)	0.031	0.548	0.047	0.665
52.3	0.906	0.262 (0.317)	0.294 (0.338)	0.278 (0.328)	-12.4 (-6.8)	-5.7 (-3.7)	0.032	0.336	0.031	0.451
683.68	0.906	1.319 (0.423)	1.289 (0.415)	1.258 (0.405)	2.3 (3.3)	4.9 (5.7)	0.032	0.609	0.047	0.699
52.18	0.97	0.331 (0.531)	0.382 (0.623)	0.357 (0.604)	-15.4 (-17.3)	-7.2 (-13.8)	0.047	0.293	0.046	0.371
195.85	0.97	0.850 (0.608)	0.909 (0.650)	0.905 (0.644)	-7.0 (-7.0)	-6.1 (-6.0)	0.032	0.375	0.031	0.478
684.88	0.97	1.820 (0.692)	1.826 (0.691)	1.814 (0.683)	-0.3 (0.0)	0.3 (1.3)	0.047	0.461	0.047	0.574
1396.82	0.97	2.539 (0.717)	2.511 (0.711)	2.467 (0.702)	1.1 (0.9)	2.9 (2.1)	0.032	0.540	0.062	0.575

Notes:

$$q\% = 100(q_{\text{exp}} - q_{\text{calc}}) / q_{\text{exp}}; \quad x\% = 100(x_{\text{exp}} - x_{\text{calc}}) / x_{\text{exp}}$$

min IAST= minimized IAST equations

trad. IAST= IAST equations solved with the traditional approach (Do, 1998; Myers and Valenzuela 1986; Valenzuela and Myers, 1989)

These results are presented in order to evaluate the advantage of the proposed solution method compared with the conventional approach of Myers (Myers and Valenzuela, 1986; Valenzuela and Myers, 1989) and

Do (Do, 1998) for the IAST equations solution. The main advantages of such new procedure are simplicity and calculation times lower than the traditional approach of about one order of magnitude which make the minimisation approach applied to binary systems adsorption comparable with the FASTIAS presented by O'Brien and Myers in (O'Brien and Myers, 1988).

Approaching the solution of eq.(8) as a minimisation problem has the following advantages: (i) it mitigates the necessity of an initial guess to apply the Newton method, substituting it with a set of initial points. This means that the solution is not affected by the closure of the initial condition to the final solution; (ii) the inversion of the spreading pressure function; (iii) the solution of an algebraic nonlinear system of equations. The problem is visualized in Figure 1 where the spreading pressure curves are plotted as a function of the molar fraction of methane.

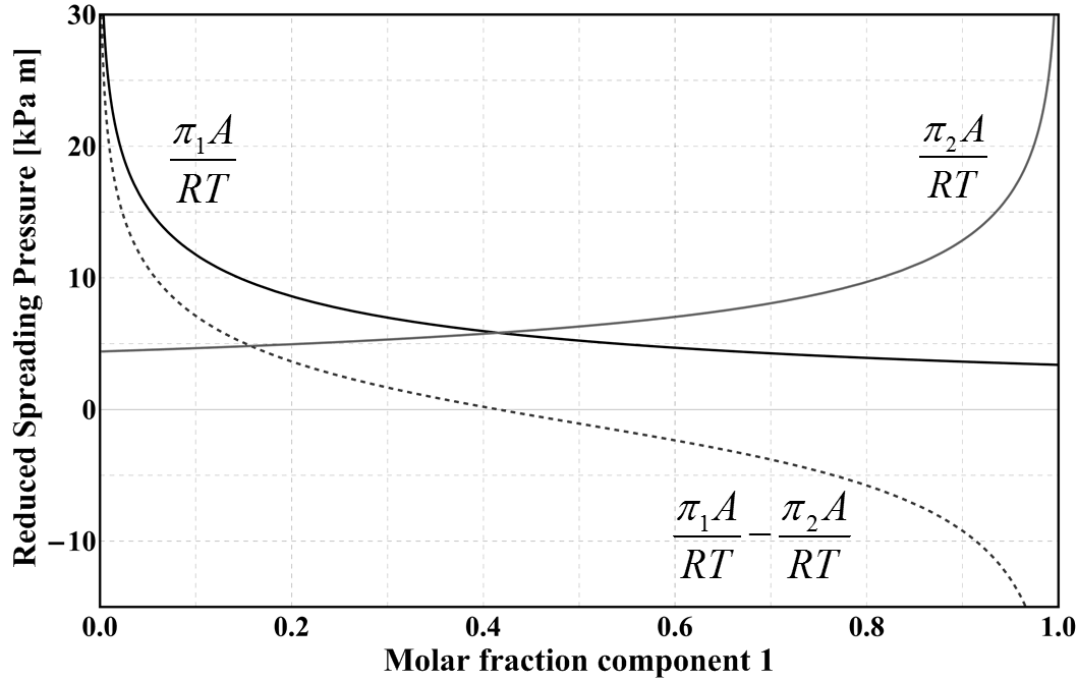


Figure 1: Reduced spreading pressure curves and reduced spreading pressure difference curve obtained using DL isotherms. The curves are calculated from the data of (He et al., 2004) for the binary system methane(1)/ethane(2) on BPL activated carbon at 301.4K, 683.68kPa and molar fraction $y_1=0.906$.

The equilibrium is represented by the value of the molar fraction where the spreading pressure difference curve has zero value. Because of high nonlinearity of the spreading pressure curves, it is more convenient to adopt a minimisation algorithm instead of trying to solve numerically the equation. Moreover, adopting eq. (8) instead of the difference curve the objective function assumes only one minimum. So even local optimization algorithms are suitable to find the correct solution.

3.2 Ternary systems

Unilan and O'Brien and Myers (OM) isotherms are used for the calculation of adsorption equilibrium in ternary systems. The system Methane(1)/Ethane(2)/Ethylene(3) on activated carbon BPL (O'Brien and Myers, 1985) was studied with the OM isotherm and the system Methane(1)/Nitrogen(2)/Carbon Dioxide(3) on activated carbon Norit R1 (Dreisbach et al., 1999) with the Unilan isotherm. This first system enables a direct comparison between the FASTIAS solution method reported in (O'Brien and Myers, 1988) and the approach proposed here, in terms of calculation times. Table 5 collects the results of the calculations.

Table 5: Methane(1)/Ethane(2)/Ethylene(3) adsorption on BPL Activated Carbon at 301.4 K (O'Brien and Myers, 1985) and Methane(1)/Nitrogen(2)/Carbon Dioxide(3) on activated carbon Norit R1 at 298 K (Dreisbach et al., 1999). Experimental data and results from the calculation of IAST equations using Unilan and O'Brien and Myers isotherms.

Pressure [kPa]	y ₁	y ₂	q ₁ (x ₁)	q ₂ (x ₂)	q ₁ (x ₁)	q ₂ (x ₂)	Errors		Calculation times [s]			
							calculated values	q ₁ % (x ₁ %)	q ₂ % (x ₂ %)	min IAS	trad IAS	FASTIAS
Methane(1)/Nitrogen(2)/Carbon Dioxide(3)												
					Unilan							
113	0.445	0.504	0.511 (0.553)	0.199 (0.215)	0.566 (0.612)	0.191 (0.181)	-10.8 (-10.7)	15.8 (15.8)	0.203	0.150	--	
433	0.535	0.125	1.469 (0.415)	0.060 (0.017)	1.200 (0.333)	0.071 (0.020)	18.3 (19.7)	-18.4 (-16.3)	0.249	0.343	--	
467	0.349	0.403	0.942 (0.298)	0.228 (0.072)	0.930 (0.291)	0.274 (0.086)	1.2 (2.3)	-20.3 (-18.9)	0.218	0.396	--	
1054	0.538	0.115	1.994 (0.361)	0.077 (0.014)	1.760 (0.310)	0.091 (0.016)	11.8 (14.2)	-17.5 (-14.2)	0.234	0.604	--	
Methane(1)/Ethane(2)/Ethylene(3)												
					O'Brien and Myers							
339.2	0.624	0.174	0.493 (0.156)	0.231 (0.469)	0.411 (0.134)	1.491 (0.484)	16.6 (14.4)	-0.6 (3.3)	0.156	0.613	0.037	
124.1	0.2	0.192	0.049 (0.019)	0.014 (0.278)	0.064 (0.024)	0.821 (0.312)	-29.4 (27.0)	-14.3 (12.2)	0.156	0.422	0.043	
131.7	0.23	0.52	0.059 (0.021)	0.044 (0.747)	0.068 (0.025)	2.055 (0.736)	-16.4 (16.8)	1.7 (1.4)	0.156	1.619	0.042	

Notes:

$$q\% = 100(q_{\text{exp}} - q_{\text{calc}})/q_{\text{exp}}$$

$$x\% = 100(x_{\text{exp}} - x_{\text{calc}})/x_{\text{exp}}$$

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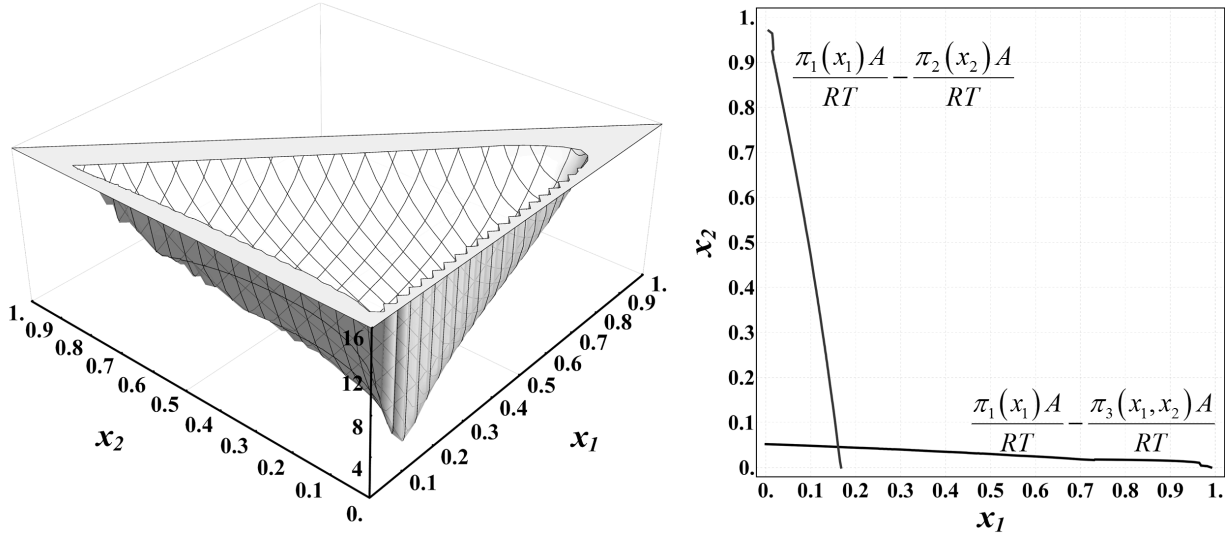
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Similarly to the binary equilibrium, the ternary equilibrium can be described by the objective function of eq. (7). This objective function is a surface which, after the substitution of eq. (2), is a function of two independent molar fractions (x_1 , x_2). Figure 2 shows an illustrative example of objective function surface. It is convex and it has only a minimum whose coordinates are the equilibrium compositions. Because of the absence of additional local minima, also in this case the objective function can be easily explored by whatever local or global minimisation algorithm. A different representation of the problem is reported also in Fig. 3, where the reduced spreading pressure difference curves are shown. The intersection point of the two curves identifies the equilibrium compositions.



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Figure 2: Objective function of eq. (7) (left) and reduced spreading pressure difference curves ($\pi_1 - \pi_2$) and ($\pi_2 - \pi_3$) (right) calculated using the Unilan isotherm for the ternary system Methane(1)/Nitrogen(2)/Carbon Dioxide(3) on activated carbon Norit R1 (Dreisbach et al. 1999) at 467kPa, 298K and compositions of the gaseous mixture (0.349; 0.403; 0.248).

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The advantage of the presented procedure over the traditional one consists also in shorter computational times even if the FASTIAS method of solution remains the fastest solution. The computational speed assumes a fundamental importance when the IAST equations are applied to the dynamic modelling of adsorbent beds where the equilibrium calculations must be repeated for several time steps (Rubiera Landa et al. 2013; Santos et al. 2011).

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As reported in Table 4 and Table 5, the calculation times are lower than the times required by the traditional solution approach, comparable to FASTIAS approach for binary mixtures adsorption and higher up to 4.2 times than the FASTIAS approach for ternary mixtures adsorption. However these times could be further reduced selecting more effective minimisation algorithms tailored on this specific problem.

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4. Conclusions

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An alternative procedure for the solution of the IAST equations was proposed. The procedure is based on the minimisation of the iso-spreading pressure condition and leads to values close to the experimental equilibrium concentrations without any involvement of spreading pressure inversion and initial guess, which are the typical requirements of the presently adopted solution approaches.

223 The procedure was tested on binary and ternary systems adsorption using Dual Langmuir, Toth, Unilan and
 224 O'Brien and Myers isotherms. A comparison with the most used existing solution procedures was presented
 225 in terms of calculation times which are fundamental in theoretical studies of adsorbent bed dynamics.
 226 In terms of calculation times, the proposed solution procedure is quicker than the traditional solution method
 227 (Do, 1998; Myers and Valenzuela 1986; Valenzuela and Myers, 1989). Calculation times become
 228 comparable to the FASTIAS method (O'Brien and Myers, 1988) for binary systems adsorption.
 229

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 234

235 **6. Nomenclature**

236	P	Pressure [kPa]
237	P_{tot}	Total pressure of the non-adsorbed mixture [kPa]
238	P_i^0	Surface pressure of the component i [kPa]
239	y_i	Molar fraction of the component i in the non-adsorbed mixture
240	x_i	Molar fraction of the component i in the adsorbed mixture
241	q_i^0	Specific amount adsorbed of component i in the adsorbent at equilibrium [mol/kg]
242	π_i^0	Spreading pressure of the component i at equilibrium [kPa m]
243	A	Specific surface area covered by the adsorbed mixture [m ² /kg]
244	R	Universal gas constant [kJ/(mol K)]
245	T	Equilibrium temperature [K]
246	NC	Number of components participating in the adsorption
247	q_i	Specific amount adsorbed of component i in the adsorbent [mol/kg]
248	q_{tot}	Specific amount adsorbed of mixture [mol/kg]
249	f_{binary}	Objective function in the case of binary mixture
250	$f_{ternary}$	Objective function in the case of ternary mixture

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